

## 11. Dissolution of Metal Sulfides & the Role of Bacteria in Production of Acid Mine Drainage

### LEACHING OF PYRITE BY ACIDOPHILIC HETEROTROPHIC IRON-OXIDIZING BACTERIA IN PURE AND MIXED CULTURES

Bacelar-Nicolau, Paula; Johnson, D. Barrie

Applied and Environmental Microbiology, Vol 65 No 2, p 585-590, Feb 1999

Seven strains of heterotrophic iron-oxidizing acidophilic bacteria were examined to determine their abilities to promote oxidative dissolution of pyrite ( $\text{FeS}_2$ ) when they were grown in pure cultures and in mixed cultures with sulfur-oxidizing *Thiobacillus* spp. Only one of the isolates (strain T-24) oxidized pyrite when it was grown in pyrite-basal salts medium. However, when pyrite-containing cultures were supplemented with 0.02% (wt/vol) yeast extract, most of the isolates oxidized pyrite, and one (strain T-24) promoted rates of mineral dissolution similar to the rates observed with the iron-oxidizing autotroph *Thiobacillus ferrooxidans*. Pyrite oxidation by another isolate (strain T-21) occurred in cultures containing between 0.005 and 0.05% (wt/vol) yeast extract but was completely inhibited in cultures containing 0.5% yeast extract. Ferrous iron was also needed for mineral dissolution by the iron-oxidizing heterotrophs, indicating that these organisms oxidize pyrite via the "indirect" mechanism. Mixed cultures of three isolates (strains T-21, T-23, and T-24) and the sulfur-oxidizing autotroph *Thiobacillus thiooxidans* promoted pyrite dissolution; since neither strains T-21 and T-23 nor *T. thiooxidans* could oxidize this mineral in yeast extract-free media, this was a novel example of bacterial synergism. Mixed cultures of strains T-21 and T-23 and the sulfur-oxidizing mixotroph *Thiobacillus acidophilus* also oxidized pyrite but to a lesser extent than did mixed cultures containing *T. thiooxidans*. Pyrite leaching by strain T-23 grown in an organic compound-rich medium and incubated either shaken or unshaken was also assessed. The potential environmental significance of iron-oxidizing heterotrophs in accelerating pyrite oxidation is discussed.

### SURFACE CHARGE DEVELOPMENT ON TRANSITION METAL SULPHIDES: AN ELECTROKINETIC STUDY

Bebié, J.; M.A.A. Schoonen; D.R. Strongin; M. Fuhrmann

Geochimica Cosmochimica Acta, Vol 62 No 4, p 633-642, 1998

### SURFACE OXIDATION OF PYRITE AS A FUNCTION OF PH

Bonnissel-Gissinger, Pascale; Marc Alnot; Jean-Jacques Ehrhardt; Philippe Behra

Environmental Science & Technology, Vol 32 No 19, p 2839-2845, 1998

Oxidation of pyrite is characterized from pH 2.5 to pH 12 by X-ray photoelectron spectroscopy and aqueous analyses of sulfur and iron.

### PYRITE-INDUCED FORMATION OF HYDROGEN PEROXIDE IN ANOXIC SOLUTIONS

Borda, M.; M.A.A. Schoonen; D.R. Strongin

EOS, [abstract only] 2000

### XPS AND LEED STUDY OF A SINGLE-CRYSTAL SURFACE OF PYRITE

Chaturvedi, S.; R. Katz; J. Guevremont; M.A.A. Schoonen; D.R. Strongin  
American Mineralogist 81, 261-264, 1996

FREQUENCY DISTRIBUTION OF THE PH OF COAL-MINE DRAINAGE IN PENNSYLVANIA  
Cravotta III, C.A. (U.S. Geological Survey, Lemoyne, PA); K.B.C. Brady; A.W. Rose; J.B. Douds  
U.S. Geological Survey Toxic Substances Hydrology Program: Proceedings of the Technical Meeting, 8-12  
March 1999, Charleston, South Carolina. Volume 1: Contamination From Hard-Rock Mining  
U.S. Geological Survey Water-Resources Investigation Report 99-4018A, p 313-324, 1999

The pH of coal-mine drainage in Pennsylvania has a bimodal frequency distribution, with modes at pH 2.5 to 4 (acidic) and pH 6 to 7 (near neutral). Although iron-disulfide and calcareous minerals comprise only a few percent, or less, of the coal-bearing rock, these minerals are highly reactive and are mainly responsible for the bimodal pH distribution. Field and laboratory studies and computer simulations indicate that pH will be driven toward one mode or the other depending on the relative abundance and extent of weathering of pyrite ( $\text{FeS}_2$ ; acid-forming) and calcite ( $\text{CaCO}_3$ ; acid-neutralizing). The pH values in the near-neutral mode result from carbonate buffering ( $\text{HCO}_3^-/\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-/\text{CaCO}_3$ ) and imply the presence of calcareous minerals; acid produced by pyrite oxidation is neutralized. The pH values in the acidic mode result from pyrite oxidation and imply a deficiency of calcareous minerals and the absence of carbonate buffering. The oxidation of only a small quantity of pyrite can acidify pure water ( $0.012 \text{ g} \cdot \text{L}^{-1} \text{ FeS}_2$  produces  $\text{pH} \sim 4$  and  $20 \text{ mg} \cdot \text{L}^{-1} \text{ SO}_4^{2-}$ ); however, because of the log scale for pH and ion complexation ( $\text{SO}_4^{2-}/\text{HSO}_4^-$  and  $\text{Fe}^{3+}/\text{FeOH}^{2+}$ ), orders of magnitude greater oxidation is required to produce  $\text{pH} < 3$ . Laboratory leaching experiments showed that for a specific proportion of  $\text{FeS}_2:\text{CaCO}_3$ , effluents produced under variably saturated hydrologic conditions, in which oxygen availability and pyrite oxidation were enhanced, had lower pH and greater dissolved solids concentrations than effluents produced under continuously saturated conditions, in which oxygen availability and pyrite oxidation were diminished. More Info: <http://toxics.usgs.gov/pubs/wri99-4018/Volume1/index.html>

#### AN ELECTROCHEMICAL APPROACH TO STUDY THE REACTIVITY OF SULFIDE MINERALS: APPLICATION TO THE ACID ROCK DRAINAGE GENERATION

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Fifth International Conference on Acid Rock Drainage, 20-26 May 2000, Denver, CO  
Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton, CO. ISBN: 0-87335-182-7. Vol 1, p 61-73, ©2000

Results of an electrochemical study using carbon paste electrodes of pyrite and pyrrhotite samples suggest that the mineralogical impurities associated with these minerals are the determinant factor on their reactivity under alteration systems. These results were supported by mineralogical and leachate chemistry data from leach cell tests. Pyrite reactivity decreases in the presence of associated impurities due to a galvanic effect whereas pyrrhotite reactivity appears to be controlled by the formation of a passivating layer. Electrochemical responses of sulfide-bearing samples provided valuable information on the prediction of ARD generation.

#### AN ELECTROKINETIC STUDY OF SYNTHETIC GREIGITE AND PYRRHOTITE

Dekkers, M.J.; M.A.A. Schoonen

#### IRON PRECIPITATION KINETICS IN SYNTHETIC ACID MINE DRAINAGE

Diz, Harry R.; John T. Novak; J. Donald Rimstidt

Mine Water and the Environment, Vol 18 No 1, Apr 1999

To evaluate the design and operation of a new active treatment system for acid mine drainage (AMD), the behavior of ferric iron solutions after the addition of bicarbonate ions was investigated. The effects of various other factors common to AMD on the precipitation rate of iron were also studied. It was found that the rate of Fe III precipitation in synthetic AMD was not affected by the presence of Al or Mn, within the concentration ranges investigated (for Al, 0-0.01 M, for Mn, 0-0.002 M). Our experiments showed that the induction time ( $t_{ind}$ ), i.e., the time elapsed between the addition of base ions and the detection of iron precipitation, decreased with increasing iron concentration and pH but increased with increasing sulfate concentration:  $\log t_{ind} = 6.7(\pm 0.30) - 1.29(\pm 0.10) \text{ pH} + 0.94(\pm 0.07) \log [\text{SO}_4] - 0.36(\pm 0.05) \log [\text{Fe}]$ . Our results suggested that sulfate sorbed to the surface of growing iron oxyhydroxides, inhibiting their growth. This effect offers an important tool that can be used to control the precipitation of iron in AMD treatment facilities.

#### SURFACE STRUCTURAL CONTROLS ON PYRITE OXIDATION-KINETICS: AN XPS-UPS, STM, AND MODELING STUDY

Eggleston, C.M.; J.J. Ehrhardt; W. Stumm

American Mineralogist, Vol 81 Iss 9-10, p 1036-1056, 1996

#### BACTERIAL AND CHEMICAL OXIDATION OF PYRITIC MINE TAILINGS AT LOW TEMPERATURES

Elberling, B.; A. Schippers; W. Sand

Journal of Contaminant Hydrology, Vol 41, p 225-238, 2000

#### NATURAL HEAVY-METAL RELEASE BY SULPHIDE OXIDATION IN THE HIGH ARCTIC

Elberling, B.; B.R. Langdahl

Canadian Geotechnical Journal, Vol 35, p 895-901, 1998

#### OXIDATION OF {111} AND {100} PLANES OF PYRITE: EFFECTS OF SURFACE ATOMIC STRUCTURE AND PREPARATION METHOD

Elsetinow, A.R.; J.M. Guevremont; D.R. Strongin; M.A.A. Schoonen

American Mineralogist, Vol 85, p 623-626, 2000

#### POTENTIAL ROLE OF BICARBONATE DURING PYRITE OXIDATION

Evangelou, V.P.; A. Holt; A.K. Seta

Environmental Science and Technology, Vol 32 No 14, p 2084-2091, 15 Jul 1998

The need to prevent the development of acid mine drainage (AMD) by oxidation of pyrite has triggered numerous investigations into the mechanisms of its oxidation. According to Frontier molecular

orbital (FMO) theory, the surface-exposed sulfur atom of pyrite possesses an unshared electron pair which produces a slightly negatively charged pyrite surface that can attract cations such as Fe<sup>2+</sup>. Because of surface electroneutrality and pH considerations, however, the pyrite surface Fe<sup>2+</sup> coordinates OH. The authors proposed that this surface Fe<sup>2+</sup> OH when in the presence of CO<sub>2</sub> is converted to -FeCO<sub>3</sub> or -FeHCO<sub>3</sub>, depending on pH. In this study, using Fourier transform infrared spectroscopy (FT-IR) they demonstrated that such complexes form on the surface of pyrite and continue to persist even after a significant fraction of the surface Fe<sup>2+</sup> was oxidized to Fe<sup>3+</sup>. FT-IR spectra also showed the presence of two carbonyl absorption bands (1,682 and 1,653 cm<sup>-1</sup>) on the surface of pyrite upon exposure to CO<sub>2</sub> which suggested that pyrite surface carbon complexes existed in two different surface chemical environments, pointing out two potential mechanisms of pyrite surface-CO<sub>2</sub> interactions. One potential mechanism involved formation of a pyrite surface-Fe(II)HCO<sub>3</sub> complex, whereas a second potential mechanism involved formation of a pyrite surface-carboxylic acid group complex [-Fe(II)SSCOOFe-(II)].

#### PYRITE CHEMISTRY: THE KEY FOR ABATEMENT OF ACID MINE DRAINAGE

Evangelou, V.P. (Bill)

Acidic Mining Lakes: Acid Mine Drainage, Limnology, and Reclamation

Springer, New York. ISBN: 354063486X. p 197-222, c1998

#### PYRITE OXIDATION AND ITS CONTROL : SOLUTION CHEMISTRY, SURFACE CHEMISTRY, ACID MINE DRAINAGE (AMD), MOLECULAR OXIDATION MECHANISMS, MICROBIAL ROLE, KINETICS, CONTROL, AMELIORATES AND LIMITATIONS, MICROENCAPSULATION

Evangelou, V.P. (Bill)

CRC Press, Boca Raton, FL. ISBN: 0849347327. 293 pp, c1995

This book focuses on pyrite oxidation theory, experimental findings on oxidation mechanisms, and applications and limitations of amelioration technologies. The text also includes discussions on the theory and potential application of novel pyrite microencapsulation technologies for controlling pyrite oxidation.

#### MICROBIAL SULFATE REDUCTION IN ACTIVE AND ABANDONED MINE TAILINGS IMPOUNDMENTS IN THE TIMMINS AREA, ONTARIO, CANADA

Fortin, D.

Sudbury '99: Mining and the Environment II, 13-15 September, Sudbury, Ontario

Centre in Mining and Mineral Exploration Research (CIMMER), Laurentian University, Sudbury, Ontario. Vol. 1, p 137-143, 1999

#### MICROBIAL SULFATE REDUCTION WITHIN MINE TAILINGS: FORMATION OF DIAGENETIC FE-SULFIDES

Fortin, D.; T.J. Beveridge

Geomicrobiology Journal, Vol 141, p 1-21, 1997

#### ROLE OF THE BACTERIUM THIBACILLUS IN THE FORMATION OF SILICATES IN ACIDIC MINE TAILINGS

Fortin, D.; T.J. Beveridge  
Chemical Geology, Vol 141, p 235-250, 1997

#### IDENTIFICATION AND DISTRIBUTION OF ARSENIC SPECIES IN AN IRON-OXIDIZING MICROBIAL MAT COMMUNITY

Foster, Andrea L.; Roger P. Ashley; James J. Rytuba

U.S. Geological Survey, Menlo Park, CA

International Conference on Heavy Metals in the Environment, 6-10 August 2000, Ann Arbor, MI  
Elsevier Science Publishers, Oxford, UK

The recent failure of a mine tailings dam at the Lava Cap mine, Nevada City district, California, released As-rich (500-1000 ppm) particulate material to creeks and a small freshwater lake (Lost Lake) in the area. Fe-hydroxide rich microbial mats collected from a small creek near Lost Lake are enriched in arsenic approximately 1000-fold relative to the waters from which they were collected. The mat community is dominated by a sheathed bacterium (tentatively identified as *Leptothrix ochracea* on the basis of its distinct "empty drinking straw" morphology), but epifluorescence microscopy using nucleic acid probes several additional unidentified community members. Scanning electron micrographs indicate that the sheaths commonly exceed 10 microns in length and have an average diameter of 1 micron. *Leptothrix* spp. are known to oxidize Fe(II) to Fe(III), but not all members of this genus have been shown to derive energy from the process. X-ray absorption fine structure (XAFS) spectroscopic analysis (conducted in bulk without sample alteration) indicates that As occurs predominantly in the pentavalent state, that it is associated with Fe oxides, and that adsorption or coprecipitation with Fe oxides is the primary mode of association. We will present data from epifluorescence microscopy, transmission electron microscopy and molecular phylogenetic analysis to characterize the microbial community present in the mat, identify and characterize the Fe oxides present, and determine the distribution of As in mat-associated Fe oxide. In addition, we will discuss the effects of seasonal mat formation, As accumulation, and As speciation on the seasonal As fluxes from this and similar mine drainage environments.

#### SORPTION PROCESSES OF IODINE ON MINERALS

Fuhrmann, M.; S. Bajt; M.A.A. Schoonen

Applied Geochemistry, Vol 13 No 2, p 127-141, 1998

#### BIOMINERALIZATION: MICROBIOLOGICAL FORMATION OF SULFIDE MINERALS

Gould, W.D.; M. Francis; D.W. Blowes; H.R. Krouse

Biological-Mineralogical Interactions

Mineralogical Association of Canada Short Course, Vol 25, p 169-186, 1997

#### REACTIVITY OF THE (100) PLANE OF PYRITE IN OXIDIZING GASEOUS AND AQUEOUS ENVIRONMENTS: EFFECTS OF SURFACE IMPERFECTIONS

Guevremont, J. (Temple Univ., Philadelphia, PA); J. Bebié; D.R. Strongin; M.A.A. Schoonen

Environmental Science & Technology, Vol 32, p 3743-3748, 1998

#### STRUCTURE SENSITIVITY OF PYRITE OXIDATION: COMPARISON OF THE (100) AND (111)

## PLANES

Guevremont J.M. (Dept. of Chem., Temple Univ., Philadelphia, PA); A.R. Elsetinow; D.R. Strongin; J. Bebić; M.A.A. Schoonen  
American Mineralogist, Vol 83 No 11/12 Pt 1, 1353-1356, 30 Nov 1998

The interaction of atomically clean (100) and (111) crystallographic planes of FeS<sub>2</sub> with H<sub>2</sub>O vapor, O<sub>2</sub>, and a H<sub>2</sub>O/O<sub>2</sub> mixture was investigated. A combined high pressure/ultra-high vacuum (UHV) apparatus allowed the surfaces to be reacted at environmentally relevant pressures and studied with X-ray photoelectron spectroscopy (XPS) without exposure to the atmosphere. Neither surface exhibited significant reaction in pure O<sub>2</sub>. Exposure of FeS<sub>2</sub>(111) to H<sub>2</sub>O vapor resulted in significant oxidation, but under these same experimental conditions FeS<sub>2</sub>(100), H<sub>2</sub>O only reacted on nonstoichiometric regions (i.e., defects). Both surfaces showed substantial reaction in H<sub>2</sub>O/O<sub>2</sub>. The amount of FeS<sub>2</sub>(100) and FeS<sub>2</sub>(111) oxidation in the H<sub>2</sub>O/O<sub>2</sub> mixture was more than simply the sum of the reaction observed individually in pure O<sub>2</sub> and H<sub>2</sub>O. This result suggests that there is a synergy between H<sub>2</sub>O and O<sub>2</sub> in oxidizing pyrite. In all cases, the amount of oxidation that occurred on FeS<sub>2</sub>(111) was greater than on FeS<sub>2</sub>(100). The authors believe that this experimental observation is due to a higher concentration of under-coordinated Fe in the outermost surface of FeS<sub>2</sub>(111), relative to FeS<sub>2</sub>(100).

## PHOTOEMISSION OF ADSORBED XENON, X-RAY PHOTOELECTRON SPECTROSCOPY, AND TEMPERATURE-PROGRAMMED DESORPTION STUDIES OF H<sub>2</sub>O ON FeS<sub>2</sub>(100)

Guevremont, J.M.; D.R. Strongin; M.A.A. Schoonen  
Langmuir, Vol 14 No 6, p 1361-1366, 1998

The reaction of H<sub>2</sub>O with the (100) crystallographic plane of pyrite, FeS<sub>2</sub>, has been investigated in the vacuum environment with photoemission of adsorbed xenon (PAX), temperature programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). TPD data indicates that H<sub>2</sub>O desorbs from FeS<sub>2</sub>(100) in a broad range of temperatures (150 - 300 K). XPS data suggests that the vast majority of H<sub>2</sub>O that initially adsorbs on pyrite at 79 K, desorbs from pyrite during thermal annealing to 300 K. PAX, a technique that is sensitive to the short range order of a surface, has been used to elucidate the types of sites that are available on FeS<sub>2</sub>(100) for the binding of adsorbate. Within the resolution of our PAX data, the surface of FeS<sub>2</sub>(100) consists of at least two types of sites. It is proposed that these two types of sites are associated with the stoichiometric surface and defect (i.e., sulfur deficient or anion vacancy) sites. PAX further suggests that at low adsorbate coverage, H<sub>2</sub>O predominately resides on defect sites. As the coverage of H<sub>2</sub>O is increased, defect sites become saturated and additional adsorption occurs on the less reactive stoichiometric surface.

## THERMAL CHEMISTRY OF H<sub>2</sub>S AND H<sub>2</sub>O ON THE STRIATED (100) PLANE OF PYRITE: UNIQUE REACTIVITY OF DEFECT SITES

Guevremont J.M.; D.R. Strongin; M.A.A. Schoonen  
American Mineralogist, Vol 83 No 11/12 Pt 1, 1246-1255, 30 Nov 1998

The interaction of a natural face of FeS<sub>2</sub> (100), cleaned in ultra-high vacuum (UHV), with H<sub>2</sub>O and H<sub>2</sub>S has been investigated with X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and the photoemission of adsorbed xenon (PAX). PAX is insensitive to the short-range order of the surface and allows the effects of defects on the surface reactivity of FeS<sub>2</sub>(100) to be studied. PAX results suggest that both H<sub>2</sub>S and H<sub>2</sub>O bind most strongly to defect sites that the authors propose are, at least in part, sulfur anion vacancy sites. Whereas the majority of H<sub>2</sub>S adsorbate desorbs from these sites in the temperature interval of 200-300 K, H<sub>2</sub>S dissociates upon heating to 500 K into adsorbed

surface hydrogen, S, and SH. This dissociation occurs on defect sites that then release part of the dissociation fragment, which is thought to be surface hydrogen, onto other regions of the pyrite surface that are proposed to be stoichiometric FeS<sub>2</sub>. Heating to 600 K causes further reaction of S containing dissociation fragments with sulfur-deficient sites to form new surface sites that resemble FeS<sub>2</sub>. The results also suggest that surface hydrogen dissolves into the pyrite bulk upon heating to 600 K.

#### EFFECTS OF IMPERFECTIONS ON THE THERMAL CHEMISTRY OF CH<sub>3</sub>OH AND H<sub>2</sub>O ON FeS<sub>2</sub>(100): USING ADSORBED XENON AS A PROBE OF MINERAL SURFACE STRUCTURE

Guevremont, J.; D.R. Strongin; M.A.A. Schoonen  
Surface Science, Vol 391 No 1-3, p 109-224, 1997

Studies are presented that investigate the adsorption and binding of CH<sub>3</sub>OH and H<sub>2</sub>O on the atomically clean (100) crystallographic plane of pyrite, FeS<sub>2</sub>. Temperature programmed desorption (TPD) suggests that both reactants molecularly adsorb at 90 K and thermally desorb between 170 and 400 K depending on the surface coverage. Photoemission of adsorbed xenon (PAX) suggests that the surface of pyrite is heterogeneous and contains a significant fraction of defect sites that are believed to be, at least in part, anion vacancy or sulfur deficient sites. An upper limit of 0.2 is proposed for the fraction of surface sites that are defects on FeS<sub>2</sub>(100). PAX indicates that these defect sites at low adsorbate coverage serve as the exclusive binding sites for H<sub>2</sub>O and CH<sub>3</sub>OH adsorbate. We speculate, on the basis of our ability to interpret PAX data for pyrite, that PAX may be of use for understanding the effect of short range order on adsorbate binding on other complex mineral surfaces. On the basis of high resolution electron energy loss spectroscopy (EELS), it is found that some dissociation of the adsorbate occurs on the pyrite. Vibrational data obtained with this technique suggests that Fe-O species result from the adsorbate decomposition. After saturation of the defect sites further molecular adsorption is accommodated on the less reactive surface that we postulate is largely disulfide, the characteristic structural group of pyrite.

#### SURFACE REACTIVITY OF PYRITE: EFFECTS OF SURFACE IMPERFECTIONS ON FeS<sub>2</sub> (100)

Guevremont, J.; D.R. Strongin; M.A.A. Schoonen; J. Bebie  
ACS National Meeting, San Francisco, 13-17 April 1997. Div. Of Geochemistry. Abstract No 140

#### EXPERIMENTAL STUDY ON THE FORMATION OF HEAVY METAL SULPHIDES USING LAYER SILICATES: ENVIRONMENTAL ASPECTS

Helios, E.; A. Rybicka; S. Piestrzynski; T. Schmidt  
Natural Microporous Materials in Environmental Technology  
Kluwer Academic Publishers, Boston. NATO science series. Series E, Applied sciences; Vol 362. ISBN: 0792358880. p 137-146, c1999

#### FERRIC IRON COMPLEXATION BY ORGANIC LIGANDS IN MINE WASTES

Herbert, R.B., Stockholm Univ., Stockholm, Sweden  
Fifth International Conference on Acid Rock Drainage, 20-26 May 2000, Denver, CO  
Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton, CO. ISBN: 0-87335-182-7. Vol 1, p 83-86, ©2000

Surface water samples were collected from water accumulations at the surface of a neutral pH mine tailings deposit in Kristineberg (Sweden) where algal growth and iron hydroxide precipitates were

observed. Ferric iron in the aqueous samples was determined by (adsorptive) differential pulse - cathodic stripping voltammetry. The analyses indicated that labile Fe<sup>3+</sup> concentrations were in the range <20 to 337 nM, while total Fe<sup>3+</sup> levels were much higher at 0.9 to 8.3 µM. The labile Fe<sup>3+</sup> levels are more than two orders of magnitude greater than would be expected based on equilibrium with ferrihydrite. These results suggest that iron complexation with strong ligands in the surface water competes with iron hydrolysis, and that these ligands may be of algal and/or bacterial origin.

#### MAGNETISM AND MAGNETO-STRUCTURAL EFFECTS IN TRANSITION-METAL SULPHIDES Hobbs, D.; J. Hafner

Journal of Physics: Condensed Matter, Vol 11 No 42, p 8197-8222, 25 Oct 1999

Recent density-functional studies of the structural and electronic properties of a wide range of transition-metal sulphides (Raybaud P, Kresse G, Hafner J and Toulhoat H 1997 J. Phys.: Condens. Matter 9 11 085, 11 107) are extended to consider the effect of magnetic ordering in sulphides formed by 3d transition metals. We find that CrS is well described as an itinerant antiferromagnet and that the magnetic ordering leads to a substantial increase of the equilibrium volume and a reduction in the axial ratio of the NiAs-type lattice. MnS(NaCl structure) is correctly described as a high-spin type-II antiferromagnet (AFM) with a very large magneto-volume effect, but the semiconducting gap is underestimated - probably due to the neglect of correlation effects. Correlation effects are also important for stabilizing the high-spin AFM type-III state of MnS<sub>2</sub> over the low-spin state. The phase transitions between non-magnetic (NM) NiAs-type FeS and antiferromagnetic troilite are well described by spin-density-functional theory, but the formation of a semiconducting gap and the magnitude of the magnetic moments and exchange splitting can be explained only by postulating correlation effects of intermediate strength. FeS<sub>2</sub> (pyrite or marcasite) and CoS are predicted to be non-magnetic, while cubic CoS<sub>2</sub> is well characterized as an itinerant weak ferromagnet. NiS and NiS<sub>2</sub> are predicted to be non-magnetic by local spin-density theory, in contrast to experiment.

#### MINERALOGICAL REACTIONS IN LYSIMETERS CONTAINING TAILINGS WITH DIFFERENT SULFIDE CONTENTS

Jambor, J.L.; L.A. Groat; S.C. Shaw; D.W. Blowes; C.J. Hanton-Fong (1999)

The paper is available at <http://www.infomine.com/rgroup/rgc/papers/ssmineralogical.pdf>

#### THE ENVIRONMENTAL GEOCHEMISTRY OF SULFIDE MINE-WASTES

Jambor, J.L.; D.W. Blowes (eds,)

Mineralogical Association of Canada. Short Course Handbook Vol 22, 1994

#### SORPTION PROPERTIES OF SECONDARY IRON PRECIPITATES IN OXIDIZED MINING WASTE

Jonsson, J.; L. Lovgren, Umea Univ., Umea, Sweden

Fifth International Conference on Acid Rock Drainage, 20-26 May 2000, Denver, CO

Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton, CO. ISBN: 0-87335-182-7. Vol 1, p 115-124, ©2000

Heavy metals may be retained within deposits of sulfide minerals under oxidation and in the nearest recipients of drainage water by sorption to secondary iron precipitates. The extent of sorption is



strongly influenced by solution pH and presence of complexing ligands, such as sulfate and natural organic acids. Desorption of metals and organic/inorganic anions to recent secondary Fe precipitates, collected at the Kristineberg mine, Sweden, has been investigated under different geochemical conditions. Elemental composition and structural characterization (X-ray powder diffraction) indicate presence of schwertmannite. While metals such as Ni and Pb were fractionally desorbed from the precipitates under acidic conditions, oxyanions, e.g. arsenate/arsenite and sulfate were desorbed preferably under alkaline conditions. In a separate study the adsorption of NOM onto synthetic goethite was investigated. NOM adsorption showed a strong pH dependence, 95% was adsorbed at pH 3 and 40% was adsorbed at pH 9. Addition of 2 mM of sulfate desorbed about 10% of the adsorbed NOM.

#### FIELD DETERMINATION OF $\text{Fe}^{2+}$ OXIDATION RATES IN ACID MINE DRAINAGE USING A CONTINUOUSLY-STIRRED TANK REACTOR

Kirby, C.S.; J.A.E. Brady

Applied Geochemistry, Vol 14, p 509-520, 1998

#### PREDICTION AND CONTROL OF BACTERIAL ACTIVITY IN ACID MINE DRAINAGE

Kwong, E.C.M.; J.M. Scharer; J.J. Byerley; R.V. Nicholson

Sudbury '95: Mining and the Environment, 28 May-1 June, Sudbury, Ontario, Canada

Canada Centre for Mineral and Energy Technology (CANMET), Ottawa, ON. Vol I, p 211-216, 1995

#### TEMPERATURE CHARACTERISTICS OF IRON SOLUBILISATION AND $^{14}\text{C}$ ASSIMILATION IN NATURAL EXPOSED ORE MATERIAL [sic] AT CITRONEN FJORD, NORTH GREENLAND (83°N)

Langdahl, B.R.; K. Ingvorsen

FEMS Microbial Ecology, Vol 23, p 275-283, 1997

#### AN INVESTIGATION OF THE PARTITIONING OF METALS IN MINE WASTES USING SEQUENTIAL EXTRACTIONS

Leinz, R.W.; S.J. Sutley; G.A. Desborough; P.H. Briggs, U.S. Geological Survey, Denver, CO

Fifth International Conference on Acid Rock Drainage, 20-26 May 2000, Denver, CO

Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton, CO. ISBN: 0-87335-182-7. Vol 2, p 1489-1500, ©2000

The mode of occurrence of metals in mine wastes is investigated using sequential extractions. Metals are extracted from some or all of seven operationally-defined phases: water-soluble, ion-exchangeable, carbonate, amorphous Fe-oxide, crystalline Fe-oxide, sulfide, and silicate. The quantity of metals extracted from each phase varies with particle size. The presence of jarosite (potassium end-member formula,  $\text{KFe}_3[\text{SO}_4]_2[\text{OH}]_6$ ) influences the selection of the procedure for extracting the crystalline Fe-oxide phase. Anglesite ( $\text{PbSO}_4$ ) and cerussite ( $\text{PbCO}_3$ ) are extracted as several phases. Extraction results can be explained only in part by X-ray diffraction (XRD) mineralogy because of lack of specificity of the extraction procedures, relatively high XRD detection limits, and the presence of 40% XRD-amorphous matter in each waste. The increasing chemical strength of the sequentially applied methods provides a basis for judging metal availability, water-soluble metals being most available and silicate-bound metals being least available.

## LABORATORY STUDIES OF PYRRHOTITE OXIDATION

MEND Secretariat CANMET, Ottawa, Ontario. MEND Report 1.21.2 , Mar 1998

Pyrite and pyrrhotite are the most abundant sulphides in mine wastes worldwide. While there is a large body of information related to the weathering of pyrite and the effects of this process on water quality, there is a significant deficiency of information on the weathering reactions and the controls on pyrrhotite reaction rates. Unlike pyrite, pyrrhotite represents a range of chemical composition as indicated by the formula  $\text{Fe}_{1-x}\text{S}$  in which  $x$  can vary from 0 to 0.125. This also implies that there is an inherent deficiency of iron in the crystal structure, possibly representing less structural stability than that of pyrite. Several crystallographic forms of pyrrhotite are known. The objectives of this investigation were to assess the kinetic controls on pyrrhotite oxidation; investigate the effects of crystal structure, metal impurities, surface area, and bacterial catalysis on oxidation reaction rates; assess the dynamics and effects on water quality of pyrrhotite oxidation in tailings column studies; and develop a modeling approach consistent with the mechanisms and controls on pyrrhotite oxidation reactions.

## INTERNET CASE STUDY FOR MAY 2000: SULPHIDE OXIDATION AND METAL LEACHING IN PERMAFROST AREAS OF GREENLAND AND CANADA

Morin, K.A.; N.M. Hutt

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Regions of continuous permafrost in the High Arctic are sometimes assumed to be free of risk for acidic drainage and significant metal leaching. Such assumptions arise from the expectation that freezing conditions will halt oxidation and associated reactions. However, laboratory and field studies have shown for decades that significantly acidic drainage arises in the High Arctic. This Internet Case Study summarizes two recent studies to complement the findings of several others. For additional information: <http://www.mdag.com/cs5-00.htm>

## INTERNET CASE STUDY FOR NOVEMBER 1998: CONTRIBUTION OF BACTERIA TO SULPHIDE-MINERAL REACTION RATES IN NATURAL ENVIRONMENTS

Morin, K.A.; Nora M. Hutt

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It is worthwhile to review recent studies related to bacterial effects, to see what the latest information is saying about bacterial contributions of sulphide minerals under natural environment conditions. There is little doubt that bacteria are present everywhere in the environment - this is well known to the medical sciences. In fact, there is actually no way to preclude or completely eradicate bacteria in minesite components, like a mined-rock pile or tailings. So the key question is whether they accelerate sulphide-mineral reaction rates under certain conditions, like within a specific pH range. The actual contribution of bacteria to reaction rates of sulphide minerals and, in fact, for all minerals can be important to the assessment, prediction, and control of minesite-drainage chemistry. Fortunately, the current ambiguous situation can be simplified by noting that, whatever the bacterial contribution, it seems to be relatively constant across most natural conditions. In effect, it mimics a mathematical constant that is always present and therefore does not have to be adjusted or quantified in many cases. For additional information: <http://www.mdag.com/cs11-98.htm>

## INTERNET CASE STUDY FOR MAY 1998: UPSIDE-DOWN OXIDATION PROFILE IN SULPHIDE-BEARING TAILINGS

Morin, K.A.; Nora M. Hutt

This Internet case study (©1998) was developed from information in Environmental Geochemistry of Minesite Drainage: Practical Theory and Case Studies

Unlike other minesite components like coarse mined-rock piles and fractured minewalls, fine-grained tailings often weather more uniformly from the outer surface, which is exposed to air and water, inward. This creates the well documented, often vertically oriented, weathering and geochemical profile of (1) the outermost tailings being most weathered and sometimes completely depleted of some primary (original) minerals, (2) a deep unweathered mass still retaining most primary minerals, and (3) an intermediate zone where active weathering is taking place. Where sulphide minerals are involved, the outermost oxidized zone is virtually depleted of sulphide minerals, the deeper intermediate zone contains actively oxidizing sulphide minerals and is migrating downwards, and the deepest unoxidized zone contains sulphide minerals not subjected to any significant oxidation. The depth to the unoxidized zone is a consequence of oxygen not reaching the deep sulphide minerals due to the full consumption of oxygen in the overlying zones and/or a water table minimizing the transport of oxygen to the unoxidized zone. As overlying sulphide minerals are consumed, oxygen can reach deeper into the tailings and thus the depth to the top of the unoxidized zone would increase with time. Due to oxygen-transport mechanisms, the rate of downward migration of the unoxidized zone slows with time and asymptotically approaches zero. For additional information: <http://www.mdag.com/cs5-98.htm>

## INTERNET CASE STUDY FOR JULY 1998: MOTHERHOOD, APPLE PIE, AND CONTAMINANT SOURCE REDUCTION

Morin, K.A.; Nora M. Hutt

This Internet case study (©1998) was developed from information in Environmental Geochemistry of Minesite Drainage: Practical Theory and Case Studies.

Much like motherhood and apple pie, attempts at reducing contaminant concentrations at the source would seem to be unquestionably of great value. However, this is not necessarily so. This month's Internet Case Study will show how attempts to reduce drainage concentrations can lead to worse and longer-term problems. Mined-rock piles with fine-grained solid covers (clay, silt, etc.) will be used as examples. To understand the conditions under which source reduction can lead to a worse problem, two basic concepts must be understood: 1) slowly vs. rapidly leachable metal and 2) equilibrium vs. kinetic reactions. The first is based on the shrinking-core model, which explains that metals at the surface of a particle will leach into water faster than metals further inside the particle. As a result, the amount of a metal in a particle can be simplistically separated into the "rapidly leachable" amount near the surface and the "slowly leachable" amount deeper inside. The finer the rock, the greater the proportion of a metal in the rapidly leachable category. For additional information: <http://www.mdag.com/cs7-98.htm>

## PYRITE OXIDATION AT CIRCUMNEUTRAL PH

Moses, C.O; J.S. Herman

Geochimica et Cosmochimica Acta, Vol 552, p 471-482, 28 Feb 1991

Previous studies of pyrite oxidation kinetics have concentrated primarily on the reaction at low pH, where Fe(III) has been assumed to be the dominant oxidant. Studies at circumneutral pH, necessitated by effective pH buffering in some pyrite oxidation systems, have often implicitly assumed that the dominant oxidant must be dissolved oxygen (DO), owing to the diminished solubility of Fe(III). In fact, Fe(III) is an

effective pyrite oxidant at circumneutral pH, but the reaction cannot be sustained in the absence of DO. The purpose of this experiment study was to ascertain the relative roles of Fe(III) and DO in pyrite oxidation at circumneutral pH.

#### OXIDATION STATES AND SPECIATION OF SECONDARY PRODUCTS ON PYRITE AND ARSENOPYRITE REACTED WITH MINE WASTE WATERS AND AIR

Nesbitt, H.W.; I.J. Muir

Mineralogy and Petrology, Vol 62, p 123-144, 1998

#### RATE OF PYRITE BIOLEACHING BY THIOBACILLUS FERROOXIDANS: RESULTS OF AN INTERLABORATORY COMPARISON

Olson, G.J.

Applied and Environmental Microbiology, Vol 573, p 642-644, 31 Mar 1991

Ten laboratories participated in an interlaboratory comparison of determination of bioleaching rates of a pyrite reference material. A standardized procedure and a single strain of Thiobacillus ferrooxidans were used in this study. The mean rate of bioleaching of the pyrite reference material was 12.4 mg of Fe per liter per h, with a coefficient of variation (percent relative standard deviation) of 32% as determined by eight laboratories. These results show the precision among laboratories of the determination of rates of pyrite bioleaching when a standard test procedure and reference material are used.

#### BIOENERGETIC RESPONSE OF THE EXTREME THERMOACIDOPHILE METALLOSPHAERA SEDULA TO THERMAL AND NUTRITIONAL STRESSES

Peeples, T.L.; R.M. Kelly

Applied and Environmental Microbiology, Vol 61 No 6, p 2314-2321, 30 Jun 1995

The bioenergetic response of the extremely thermoacidophilic archaeon Metallosphaera sedula to thermal and nutritional stresses was examined. Continuous cultures in which the levels of Casamino Acids and ferrous iron in growth media were reduced by a step change of 25 to 50% resulted in higher levels of several proteins. Respiratory activity, as evidenced by iron speciation in parallel temperature-shifted cultures on iron pyrite, was examined. If cultures shifted from 70 to 80 degrees C were shifted back to 70 degrees C after 4 hours, cells were able to regain pyrite oxidation capacity and internal pH increased to nearly normal levels after 13 hours. When M. sedula was subjected to an intermediate temperature shift from 73 to 79 degrees C, an increase in pyrite dissolution (ferric iron levels doubled) over that of the unshifted control at 73 degrees C was noted. The improvement in leaching was attributed to the synergistic effect of chemical and biological factors. As such, periodic exposure to higher temperatures, followed by a suitable recovery period, may provide a basis for improving bioleaching rates of acidophilic chemolithotrophs.

#### REDOX CHEMISTRY OF IRON AND SULFUR AT THE INTERFACE BETWEEN SEDIMENT AND GROUND-WATER OF ACID MINE LAKES

Peiffer, S.; A. Peine; A. Tritschler; K. Küsel

Hydrology and Chemical Processes. Restoration of Aquifers: Natural and Artificial Attenuation. Vol 3: Redox processes in aquifers

## ATMOSPHERIC OXIDATION OF THE PYRITIC WASTE ROCK IN MAARDU, ESTONIA, 2: AN ASSESSMENT OF ALUMINOSILICATE BUFFERING POTENTIAL

Puura, E.; I. Neretnieks

Environmental Geology, Vol 39 No 6, p 560-566, 18 Apr 2000

The assessment of the aluminosilicate buffering potential during acid weathering of the Estonian alum shale is provided. It is found that the stoichiometric interaction between dissolved pyrite oxidation products and illite of the shale best describe the buffering process and are consistent with earlier field studies. The scheme includes incongruent dissolution of illite with smectite and K-jarosite precipitating. This complex mechanism involves buffering of 8% of the acidity by K<sup>+</sup> and temporary precipitation of 25% of the acidity as K-jarosite. Dissolution proceeds at a low pH (1.5-3) until all pyrite in the shale particle is oxidised. Hence, if the total amount of illite present is larger than needed for stoichiometric interactions, only part of it is involved in a buffering process, neutralising a certain percentage of acidity. The next stage in shale weathering is the incongruent dissolution of K-jarosite with the release of the precipitated acidity and the formation of ferric oxyhydroxide.

## EPITAXIAL OVERGROWTHS OF MARCASITE ON PYRITE FROM THE TUNNEL AND RESERVOIR PROJECT, CHICAGO, ILLINOIS, USA: IMPLICATIONS FOR MARCASITE GROWTH

Rakovan, J.; M.A.A. Schoonen; R.J. Reeder

Geochimica et Cosmochimica Acta, Vol 59, 1995

## SULFIDE FORMATION IN RESERVOIR CARBONATES OF THE DEVONIAN NISKU FORMATION, ALBERTA, CANADA: AN ION MICROPROBE STUDY

Riciputi, L.R.; D.R. Cole; H.G. Machel

Geochimica et Cosmochimica Acta, Vol 60 No 2, p 325-336, 31 Jan 1996

The processes affecting sulfur during diagenesis in carbonates have been investigated by ion microprobe analysis of sulphur values of pyrite, marcasite, and anhydrite from the Devonian Nisku Formation in the Western Canada Sedimentary Basin. The predominately low S values of Nisku sulfides indicate bacterial sulfate reduction. Textural relations indicate that Fe-sulfide formation in Nisku carbonates may have occurred by two different mechanisms. Much of the sulfide has S values that suggest that it was associated with bacterial sulfate reduction, although most Fe-sulfides did not form until after pervasive matrix dolomitization (depths of 300-1000 m). Other sulfide may have formed later, during deep (~4km) burial via thermochemical sulfate reduction. The range in S values in a single thin section and correlations between pyrite morphology and isotopic values suggest that sulfate reduction was a very localized process, and that the sulfate reduction environment varied considerably on a small scale.

## CHEMISTRY OF IRON SULFIDES IN SEDIMENTARY ENVIRONMENTS

Rickard, D.T.; M.A.A. Schoonen

Geochemical Transformations of Sedimentary Sulfur

ACS Symposium Series Vol 612, Chap 8, 26 pp, 1995

## MARCASITE OXIDATION IN LOW TEMPERATURE ACIDIC (PH 3.0) SOLUTIONS: MECHANISM AND RATE LOWS

Rinker, M.J.; H.W. Nesbitt; A.R. Pratt  
American Mineralogist 82:900-912, 1997

#### HISTORICAL OVERVIEW AND FUTURE DIRECTIONS OF THE MICROBIAL ROLE IN THE ACIDIC COAL MINE DRAINAGE SYSTEM

Robbins, Eleanora I. (U. S. Geological Survey, Reston, VA)

Proceedings, 25th Anniversary and 15th Annual National Meeting of the American Society for Surface Mining and Reclamation, 17-21 May 1998, Saint Louis, MO

American Society for Surface Mining and Reclamation. p 174-191, 1998

Bacteria have been implicated and analyzed at every step in the production of acidic coal mine drainage (AMD). This review paper provides detailed information about microbial studies in mines, laboratory settings, waste piles, ground water, receiving streams, and downstream rivers and lakes. Research on AMD treatment, beneficial uses, and seasonal variability is also reviewed.

#### DETECTION OF MASSIVE SULFIDES AT KIDD CREEK USING LOGGING, ROCK PROPERTIES AND SEISMIC REFLECTION METHODS

Salisbury, M.H.; W. Bleeker; D. Eaton; B. Milkereit

Economic Geology, 1998

#### BACTERIAL METAL SULFIDE DEGRADATION—PATHWAYS, INHIBITION MEASURES, AND MONITORING

Schippers, A.; P.G. Jozsa; T. Gehrke; T. Rohwerder; W. Sand, Universitat Hamburg, Hamburg, Germany

Fifth International Conference on Acid Rock Drainage, 20-26 May 2000, Denver, CO

Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton, CO. ISBN: 0-87335-182-7. Vol 1, p 75-82, ©2000

Metal sulfides are degraded via thiosulfate (pyrite) or via polysulfides and sulfur (sphalerite, galena, chalcopyrite) by leaching bacteria. The attack on the crystal lattice is either effected by only iron (III) ions or by iron (III) ions and protons, respectively. Consequently, different endproducts are formed. For a control of ARD processes, these reactions need to be known to regulate them. Experiments in percolators up to 65 m<sup>3</sup> with inorganic compounds like fluoride, concrete, or SDS resulted in differently lasting inhibition. Microcalorimetric measurements of microbial leach activity allow monitoring of these effects with respect to active bacterial cells, and, in addition, the amount or rate of dissolved metal sulfide allowing prediction of possible endangerment by ARD.

#### MICROBIOLOGICAL PYRITE OXIDATION IN A MINE TAILINGS HEAP AND ITS RELEVANCE TO THE DEATH OF VEGETATION

Schippers, A.; P.-G. Jozsa; W. Sand; Z.M. Kovacs; M. Jelea

Geomicrobiology Journal, Vol 17 No 2, p 151-162, Apr 2000

The oxidation of pyrite in a mine tailings heap in Romania was studied to clarify the contribution of acid drainage to the death of vegetation on the eastern slope of the tailings. Where vegetation died, pyrite oxidation was detected as deep as 1 m, as indicated by the brownish color of the samples. At these sites *Thiobacillus ferrooxidans*-like bacteria were present with cell counts of 10<sup>3</sup> g and *Thiobacillus thiooxidans*-like bacteria occurred with cell counts of 10<sup>4</sup> g. At the western slope, where vegetation thrived,

cell counts of  $< 10^6$  g were measured. Correspondingly, leaching activity and concentrations of pyrite oxidation products such as sulfate and elemental sulfur were markedly higher on the eastern slope than on the western slope. These differences were mainly a result of the high acid neutralization potential in the material from the western slope, which kept the pH in a neutral range allowing for plant growth. In contrast, on the eastern slope with its low acid neutralization potential, the pH dropped to 3 to 4, increasing the solubility of phytotoxic elements. The death of the vegetation could result from the lowered pH and the increased amount of toxic elements, or, most likely, a combination of these factors.

#### INTERMEDIARY SULFUR COMPOUNDS IN PYRITE OXIDATION: IMPLICATIONS FOR BIOLEACHING AND BIODEPYRITIZATION OF COAL

Schippers, A.; T. Rohwerder; W. Sand

Applied Microbiology and Biotechnology, Vol 52 No 1, p 104-110, 27 Jul 1999

Accumulation of elemental sulfur during pyrite oxidation lowers the efficiency of coal desulfurization and bioleaching. In the case of pyrite bioleaching by *Leptospirillum ferrooxidans*, an iron(II)-ion-oxidizing organism without sulfur-oxidizing capacity, from the pyritic sulfur moiety about 10% elemental sulfur, 2% pentathionate, and 1% tetrathionate accumulated by a recently described cyclic pyrite oxidation mechanism. In the case of pure cultures of *Thiobacillus ferrooxidans* and mixed cultures of *L. ferrooxidans* and *T. thiooxidans*, pyrite was nearly completely oxidized to sulfate because of the capacity of these cultures to oxidize both iron(II) ions and sulfur compounds. Pyrite oxidation in acidic solutions, mediated chemically by iron(III) ion, resulted in an accumulation of similar amounts of sulfur compounds as obtained with *L. ferrooxidans*. Changes of pH to values below 2 or in the iron ion concentration are not decisive for diverting the flux of sulfur compounds. The literature on pyrite bioleaching is in agreement with the findings indicating that the chemistry of direct and indirect pyrite leaching is identical.

#### SULFUR CHEMISTRY IN METAL SULFIDE OXIDATION

Schippers, A.; W. Sand

Hamburg Univ. (Germany). Abt. Mikrobiologie

The 9th International Conference on Coal Science (ICCS '97), 7 Sep 1997, Essen, Germany

TIB Hanover. ISBN: 3-931850-22-6. Vol 3, p 1643-1646, 1997

Oxidative pyrite degradation proceeds via polythionates in a novel cyclic pathway. Elemental sulfur is only a side-product of the reactions. At neutral pH polythionates accumulate to high amounts whereas in case of bacterial leaching at acidic pH mainly sulfate besides some elemental sulfur and polythionates are formed. Oxidative degradation of sphalerite (ZnS) and galena (PbS) does not proceed via polythionates. Instead, high amounts of elemental sulfur accumulate at acidic pH, reflecting a different degradation mechanism. This can be explained by the different crystal structure and the solubility of the metal sulfides. An understanding of the mechanism of metal sulfide oxidation may help to improve measures against the detrimental impact of acid rock drainage (ARD) or to improve coal desulfurization operations.

#### GOLD SORPTION ONTO PYRITE AND GOETHITE: A RADIOTRACER STUDY

Schoonen M.A.A.; N.S. Fisher; M. Wente

Geochimica Cosmochimica Acta, Vol 56, p 1801-1814, 1992

## MINERALOGICAL STUDY OF BASE METAL TAILINGS WITH VARIOUS SULFIDE CONTENTS, OXIDIZED IN LABORATORY COLUMNS AND FIELD LYSIMETERS

Shaw, S. C.; L.A. Groat; J.L. Jambor; D.W. Blowes; C.J. Hanton-Fong; R.A. Stuparyk  
Environmental Geology, Vol 33 No 2/3, p 209-217, 25 Feb 1998

Oxidation of a flotation-derived, low-sulfide tailings containing approximately 0.4 wt.% S was compared with simultaneously oxidized tailings containing 1.0 wt.% S and 2.5 wt.% S to assess their acid generating characteristics. Each tailings type was exposed to oxidation for three years in laboratory columns and in lysimeter pits in the field. In these tailings the sulfide mineral of principal concern with respect to acid generation is pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ). In past studies the alteration of pyrrhotite has been characterized by initial replacement with marcasite ( $\text{FeS}_2$ ) and ferric iron sulfates, which are followed by development of ferric oxyhydroxides such as goethite and lepidocrocite. Macroscopic characterization of the tailings shows varying and progressive degrees of oxidation correlative with the three different sulfur contents. As expected, the tailings with the lowest sulfur content are the least oxidized, and those with the highest sulfur content have reacted the most. The column tests, which represent accelerated reaction conditions relative to those for the lysimeter pits, show much higher degrees of oxidation, and a markedly more distinct boundary between the oxidized and unoxidized zones; as well, differences among the three tailings types are more pronounced.

## MINERALIZED BACTERIAL BIOFILMS IN SULPHIDE TAILINGS AND IN ACID MINE DRAINAGE SYSTEMS

Southam, Gordan; F. Grant Ferris; Terrance J. Beveridge  
Microbial Biofilms

Cambridge University Press, Plant and microbial biotechnology research series 5. ISBN: 0521454123.  
Chapter 8, 1995

## MICROBIALY-MEDIATED REDUCTIVE DISSOLUTION OF ARSENIC-BEARING MINERALS IN A GOLD MINE TAILINGS IMPOUNDMENT

Stichbury, M.K.; J.G. Bain; D.W. Blowes (Univ. of Waterloo, Waterloo, ON); W.D. Gould (CANMET, Ottawa, ON)

Fifth International Conference on Acid Rock Drainage, 20-26 May 2000, Denver, CO

Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton, CO. ISBN: 0-87335-182-7. Vol 1, p 97-106, ©2000

The mechanisms of release of arsenic in gold mine tailings were investigated. The highest concentration of dissolved As (75 mg/L) was observed near the base of the tailings impoundment, in close association with a peat layer. Elevated concentrations of reduced iron and hydrogen sulfide were also measured at the base of the impoundment. High numbers of iron-reducing and sulfate-reducing bacteria were detected at depths within the impoundment, which correlated with dissolved As, Fe and  $\text{H}_2\text{S}$ . The data presented in this paper suggest that arsenic is released from the tailings by bacterially-mediated reductive dissolution of As-bearing iron minerals.

## CONTROLS OF $\text{I}^{18}\text{O}$ IN SULFATE

Van Stempvoort, D.R.; H.R. Krouse

Environmental Geochemistry of Sulfide Oxidation

American Chemical Society, New York. ACS Symposium Series No 550, p 446-480, 1994



## INTERFACIAL ELECTROCHEMISTRY OF PYRITE OXIDATION AND FLOTATION. 1: EFFECT OF BORATE ON PYRITE SURFACE OXIDATION

Wang, X.H.

Journal of Colloid and Interface Science, Vol 178 No 2, p 628-637, 25 Mar 1996

The interfacial chemistry of pyrite is of great industrial importance in complex sulfide ore flotation, coal desulfurization, acid mine drainage mitigation, and conversion of solar energy to electrical or chemical energy. Sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ) has been widely used as an electrolyte and pH buffer in studying the interfacial electrochemistry of sulfide minerals in relation to sulfide mineral flotation. In all the previous studies published so far, borate was regarded as an inert electrolyte/pH buffer, and its reactions with the sulfide minerals were completely overlooked. In this first part of this series papers, the complicating effects of borate on the interfacial electrochemistry of pyrite have been studied. In the borate solutions, the surface oxidation of pyrite is strongly enhanced. The first and rate-determining step of the reaction between borate and pyrite has been shown to be an irreversible reaction. The reaction appears in the voltammogram as an anodic oxidation peak at potentials of more than 0.4 V lower than the commencement of pyrite oxidation in sodium perchlorate or nitrate electrolyte solutions. As the borate concentration increases, the peak current increases linearly, while the peak potential shifts positively at 240 mV per decade. On a rotating-disc electrode, the peak becomes a plateau. The limiting current density is a linear function of the square root of the rotation speed at relatively low rotation speeds. The Tafel slope is close to 240 mV per decade and is independent of the rotation speed and borate concentration. The results indicate that charge transfer coefficient is 0.25.

## INTERFACIAL ELECTROCHEMISTRY OF PYRITE OXIDATION AND FLOTATION. 2: FTIR STUDIES OF XANTHATE ADSORPTION ON PYRITE SURFACES IN NEUTRAL PH SOLUTIONS

Wang, X.H.

Journal of Colloid and Interface Science, Vol 171 No 2, p 413-428, 31 May 1995

Infrared spectra of short carbon chain ferric xanthates were systematically characterized and compared with that of their corresponding alkali xanthates and dixanthogens. Ferric xanthates display an intense absorption band at the frequencies of 1,260--1,235  $\text{cm}^{-1}$  (in KBr), depending on the carbon number of the alkyl chain. The bands have been assigned to the asymmetric stretching vibration of C-O-C linkage. The absorption bands shift to lower frequencies in organic solvents like carbon tetrachloride. The position of the C-O-C bands in the corresponding dixanthogen appears at higher frequencies in the range of 1,260--1,270  $\text{cm}^{-1}$  and shows no shift in the organic solvents. The adsorption of short chain xanthates on the surfaces of synthetic high purity pyrite microcrystalline in neutral pH solutions has been investigated. Both dixanthogen and ferric xanthate characteristic IR peaks have been observed. The quantity of dixanthogen is much greater than that of ferric xanthates for all the xanthates studied. For the pyrite-ethyl xanthate system, when the xanthate-reacted pyrite is rinsed with hexane, nearly all the dixanthogen formed on the pyrite surfaces is washed away. The remaining spectrum of the washed xanthated-pyrite resembles that of the corresponding ferric xanthate. In addition, a sharp peak has been observed at 1,090  $\text{cm}^{-1}$  on the hexane-washed pyrite surfaces, possibly indicating that ethyl xanthate ions are specifically adsorbed on pyrite surfaces. These results suggest that ferric-xanthate compounds are formed in the pyrite-xanthate systems as surface compounds on the pyrite surfaces and/or as a separate precipitate phase in the bulk solution.

## A COMPREHENSIVE EMPIRICAL RATE LAW FOR AQUEOUS PYRITE OXIDATION BY

#### FERRIC IRON AND DISSOLVED OXYGEN

Williamson, M.A.; J.D. Rimstidt; W.D. Newcomb

Geological Society of America, Abstracts with Programs, Vol 247, p A209, 31 Jan 1992

The authors performed a series of batch and mixed flow reactor experiments at 25 C to determine the rate of oxidation of pyrite by ferric iron at acidic pH's. These data were combined with rate data reported by Smith and Shumate (1970) and McKibben (1984) to produce a data set of 115 measurements of pyrite oxidation rates in acidic solutions determined over the solution composition range  $0.5 < \text{pH} < 2.6$ ;  $-9.5 < \log m_{\text{Fe(III)}} < -1.0$ ;  $-5.5 < m_{\text{Fe(II)}} < -0.5$ . Multiple linear regression analysis showed that the rate of reaction was unaffected by  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and ionic strength. They propose empirical rate law for pyrite oxidation. In addition, the authors formulated another rate law using data (47 values) from Smith and Shumate (1970) and McKibben (1984) for the reaction of dissolved  $\text{O}_2$  (DO) with pyrite over the range  $-0.4 < m_{\text{DO}} < -1.75$ ;  $1.5 < \text{pH} < 10.0$ . The regression produced normally distributed residuals for both models. The rate law for Fe(III) was found to valid over 4.5 orders of magnitude of rate and the  $\text{O}_2$  rate law over 2 orders. Assuming a solution composition that is in equilibrium with  $\text{Fe}(\text{OH})_{3\text{am}}$  and atmospheric  $\text{O}_2$ , the rate of oxidation by Fe(III) is dominate for  $\text{pH} < 3.75$  while the reaction with DO is faster at higher pH's.

#### THE STABILITY OF THIOSULFATE IN THE PRESENCE OF PYRITE IN LOW-TEMPERATURE AQUEOUS SOLUTIONS

Xu, Y.; M.A.A. Schoonen

Geochim. Cosmochim. Acta, Vol 59, p 4605-4622, 1995

#### TRANSPASSIVE OXIDATION OF PYRITE

Zhu, Ximeng; D.M. Bodily; M.E. Wadsworth

Journal of the Electrochemical Society, 1927-1934, Vol 1407, p 1927-1934, 31 Jul 1993

The electrochemical behavior of mineral and coal pyrites in basic borate/sulfate solutions was investigated using cyclic voltammetry with both stationary and rotating disk electrode. Emphasis was centered on transpassive oxidation. In the transpassive region, 0.4 to 0.8 V (SCE), aggressive oxidation of pyrite occurred. The reaction products in this region are Fe(III) oxides, sulfate ion, and partially oxidized sulfur intermediates. The formation of sulfur and polysulfides was identified by in situ Raman spectroscopy. Exposure of pyrite to anodic potentials higher than the transpassive region resulted in rapid oxidation of sulfur intermediates to sulfate ion. The effect of electrode rotation speed, electrode precondition time, and upper potential of the scan in the transpassive region was observed to be critical to the formation of sulfur intermediates. Sulfur intermediates, formed in the transpassive region, dramatically affected subsequent oxidation reactions occurring in the lower potential region. The magnitude of two dominant oxidation peaks, a ferrous hydroxide peak and an iron sulfide peak, observed in this region correlated directly with the quantity of sulfur intermediates formed in the transpassive region. This effect was less pronounced for coal pyrites compared to mineral pyrite.